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WHITE PAPER

Guide to Measuring Oil Chemistry: Nitration, Oxidation and Sulfation

Background

An in-service lubricant encounters air, heat, pressure, corrosive agents, and other factors that cause chemical changes in the oil. A change in oil chemistry can affect the ability of the lubricant to do its job (for example if crucial additives have been depleted). Over time, these chemical reactions can result in build-up of harmful degradation by-products like weak organic acids. Oil chemistry analysis always includes oxidation and may also include nitration and sulfation depending on the application. In some cases, oils may also be tested to check for the depletion of specific additives, like a ZDDP antiwear package.

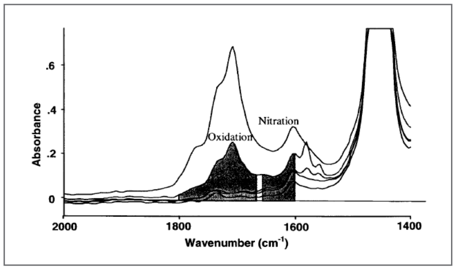
OXIDATION — Oxidation of oil occurs in the presence of air (oxygen) and heat. The atmospheric oxygen reacts with the hydrocarbons in the lubricant to form carboxylic acids. These acids are weak, but given enough time the concentration can become high enough to cause severe corrosion of machinery parts. This is an inevitable process that must be monitored. To help protect the lubricant, antioxidant additives are included in almost all formulations. The additives will oxidize readily before the more important components of the oil will oxidize. Once these additives are depleted, the lubricant properties will be negatively affected. The oxidation rate varies greatly with temperature and is also affected by any contaminants (particularly metals) present in the lubricant, so keeping the oil clean, dry, and as cool as possible is the best way to manage oxidation.

NITRATION — Nitration is of concern in engine oils, particularly natural gas engine oils. Heat can cause atmospheric nitrogen (N2) and oxygen (O2) to react, forming nitrous oxides (NOx). These nitrous oxides interact with the lubricant by creating organic nitrates or being picked up as either soluble or insoluble nitrous compounds. Nitration can cause premature thickening of the engine oil. Common causes of nitration include inefficient exhaust of the combustion products , improper air-to-fuel ratio, low operating temperature, and leaking piston seals.

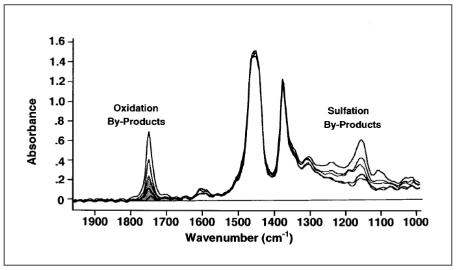
SULFATION — The reaction between oxygen, heat, water and sulfur from diesel fuel or base oil can create sulfurous compounds including sulfur based acids. Most of the time these sulfurous compounds are expelled through exhaust, but some may remain and make their way into the engine cavity. Sulfation occurs when these acids react with either the additives in the oil or the base stock of the lubricant. At lower operating temperature, such as during start up, the acids can condense and more readily come into contact with the oil. Sulfation can cause increased viscosity and the formation of varnish, sludge, and sedimentation.

Methods of Measuring Oil Chemistry

INFRARED SPECTROSCOPY



ASTM E2412 – Oxidation and nitration measurement in Crankcase Oils.



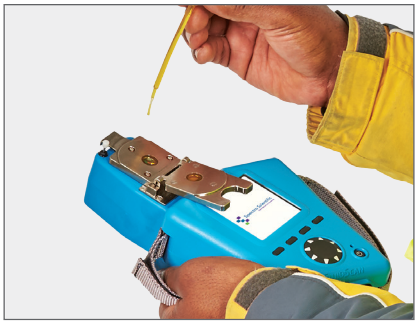
ASTM E2412 – Oxidation measurement in EP Fluids

Infrared spectroscopy uses a radiative source, a detector, and a computer to study the interaction of matter and light. Oxidation and nitration products appear as peaks in the IR spectrum between 1600 and 1800 cm^{-1}. Sulfation products appear as peaks in the IR spectrum around 1120-1180 cm^{-1}. Because there are no absolute reference standards for oxidation, nitration, and sulfation, the results are always compared to those of new oil. For example, if the nitration peak around 1650 cm^{-1} becomes significantly more intense as engine oil is sampled over a specified time, then nitration has occurred, possibly due to improper air/fuel ratio.

PROS:
- Low cost per sample after initial equipment purchase
- Test is quick
- Great for direct trending of oil chemistry properties

CONS:
- Requires expensive equipment

There are test methods for laboratory grade FTIR measurement as well as for portable field testing. ASTM E2412 describes the standard practice for FTIR measurement of these properties. In addition, specific test methods have been defined for oxidation (D7414), nitration (D7624), and sulfation (D7415). For monitoring oil chemistry in the field, ASTM D7889 uses a grating infrared spectrometer like the FluidScan® which is easy to operate and does not require an experienced technician.



FluidScan 1100

VISCOSITY

The only direct method to measure oxidation, nitration, and sulfation is by spectroscopy. Indirect methods are viscosity and impedance measurements. Viscosity is the measure of a fluid's resistance to flow. As oxidation, nitration, or sulfation occur in an oil, condensation products are formed which will cause an increase in viscosity. A change in viscosity, regardless of the cause, is a critical parameter to test for, so viscosity testing is already part of any lubricant condition monitoring program. There are many methods (ASTM D445 and ASTM 7279, among others) with instrumentation available for both lab and field testing, including the Spectro Scientific MiniVisc 3000 portable kinematic viscometer.

IMPEDANCE

Another indirect measurement for these properties is impedance testing, which measures the conductivity or dielectric properties of a fluid. These properties are strongly affected by changes in polarity of the hydrocarbons, which is particularly sensitive to oxidation due to carboxylic acids formation. The presence of other contaminants like water or other degradation byproducts will also strongly contribute to a change in impedance, so this test is typically used for trending the overall condition of oil.

Summary

Testing for oxidation, nitration, and sulfation of a lubricant allows trending of useful oil life and can also signal improper operating conditions, failure of engine parts (piston seals), or the wrong lubricant for the application. There are indirect methods of testing a lubricant's ability to perform its function, like viscosity, but the only direct method to determine whether oxidation, nitration, or sulfation is happening is to use infrared spectroscopy. FTIR instruments and methods are available for intermediate to expert users in a laboratory setting and the Spectro Scientific FluidScan allows testing for oil chemistry out in the field (or in the lab) with a portable IR spectrometer.

References

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4. ASTM E2412. Standard Practice for Condition Monitoring of In-Service Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry.
5. ASTM D7889. Standard Test Method for Field Determination of In-Service Fluid Properties Using IR Spectroscopy.

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